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**C08L 27/18****C08L 27/18**(21)Application number : **06-147149**(71)Applicant : **DU PONT MITSUI FLUOROCHEM CO LTD**(22)Date of filing : **06.06.1994**(72)Inventor : **NAMURA SHINICHI  
NISHIO TAKAO****(54) FLUOROPLASTIC POWDER COMPOSITION FOR POWDER PROCESSING****(57)Abstract:**

PURPOSE: To obtain a fluoroplastic powder composition which has excellent coating film formation and is suitable for forming coating film excellent in surface smoothness by powder processing, for example, powder coating or rotational molding.

CONSTITUTION: This perfluoroalkyl (PFA) resin powder composition comprises polytetrafluoroethylene (PTFE) particles of 50J/g or more heat of crystallization or PTFE colloidal particles of 50J/g or less heat of crystallization wherein the average particle size of the composition is 1-1,000 microns and the specific melt fluidity under no loading satisfies the expression:  $\log_{10} F \geq 3.12 - 0.70 \log_{10} \eta$  [F is unloaded melt fluidity of the copolymer powder;  $\eta$  is the specific melt fluidity of the copolymer powder at 372°C].

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention]

[0003] Since the object of this invention has the detailed spherulite which is excellent in a film plasticity and is formed at the time of crystallization, it is in offering the powder constituent of PFA which gives the paint film which was excellent in surface smooth nature with powder processing of powder coating, rotational casting, etc., and a moldings.

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TECHNICAL FIELD

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[Industrial Application] This invention relates to a fluoro-resin powder constituent useful as powder for powder processing, such as powder coating and rotational casting. Furthermore, in detail, it is the tetrafluoroethylene / perfluoro (alkoxy trifluoro ethylene) copolymer powder constituent which contains a polytetrafluoroethylene particle and changes, and is related with the fluoro-resin powder constituent suitable for obtaining a paint film and a moldings excellent in surface smooth nature.

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CLAIMS

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[Claim(s)]

[Claim 1] The polytetrafluoroethylene particle and the heat of crystallization whose heat of crystallization is 50J/g or more contain at least one sort of polytetrafluoroethylene particles chosen from the colloid polytetrafluoroethylene particle of less than 50 J/g. They are the tetrafluoroethylene / perfluoro (alkoxy trifluoro ethylene) copolymer powder constituent which changes. The mean particle diameter of this powder constituent by 1-1000 microns and the formula  $\log_{10}$  of the following [ fluidity / no-load melting ] -- the ratio of a copolymer powder constituent [ in / the inside F of a  $F \geq 3.12 - 0.70 \log_{10} \eta$  (type, and / in  $\eta$  / 372 degrees C ] -- melt viscosity (poise) is expressed. [ the no-load melting fluidity of a copolymer powder constituent ] ] The fluororesin powder constituent for powder processing characterized by being satisfied.

[Claim 2] The powder constituent according to claim 1 with which a polytetrafluoroethylene particle has the heat of crystallization 50J [ /g ] or more.

[Claim 3] The powder constituent according to claim 1 whose polytetrafluoroethylene particle is a colloid polytetrafluoroethylene particle which has the less than 50J [ /g ] heat of crystallization.

[Claim 4] The powder constituent according to claim 2 whose content of a polytetrafluoroethylene particle is 25 or less % of the weight.

[Claim 5] The powder constituent according to claim 3 whose content of a polytetrafluoroethylene particle is 1 or less % of the weight.

[Claim 6] The powder constituent according to claim 1 to 5 whose content of a polytetrafluoroethylene particle is 0.001 % of the weight or more.

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EFFECT OF THE INVENTION

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[Effect of the Invention] It comes out of the powder constituent of this invention to process it according to the same processing conditions as the conventional PFA powder for powder processing. The front face of works, such as lining or a container by which coating was carried out, a pipe, and a joint, is excellent in smooth nature with the container obtained by rotational casting, a pipe, revolution lining, or powder coating compared with the front face of the work obtained from the conventional PFA powder. Therefore, the dust particle adhering to a work front face is removable by short-time washing. Since PTFE used as an additive has thermal resistance and chemical resistance equivalent to PFA, the physical properties on the front face of a work are also excellent. Especially the work obtained from the constituent which does not contain the component eluted with drug solutions, ~~such as a metal~~, as a thermostabilizer or a filler among the constituents of this invention fits the facility for dealing with the high grade drug solution used by the semi-conductor production process which dislikes mixing of a foreign matter.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a fluororesin powder constituent useful as powder for powder processing, such as powder coating and rotational casting. Furthermore, in detail, it is the tetrafluoroethylene / perfluoro (alkoxy trifluoro ethylene) copolymer powder constituent which contains a polytetrafluoroethylene particle and changes, and is related with the fluororesin powder constituent suitable for obtaining a paint film and a moldings excellent in surface smooth nature.

[0002]

[Description of the Prior Art] Although tetrafluoroethylene / perfluoro (alkoxy trifluoro ethylene) copolymer is known for an abbreviated name called PFA, and the powder is used for rotational casting, such as paint, and lining or a container to base materials, such as iron and aluminum, since melting shaping is possible, since the front face of the paint film obtained or a moldings is not smooth, a contamination tends to adhere to a front face, and the problem that washing is also hard to remove is pointed out. The 1st factor which affects surface smooth nature is the film plasticity of polymer powder, it is known that physical properties, such as particle diameter of polymer powder, particle shape, a melting fluidity, and thermal stability, will affect a film plasticity, and many examination is already made about this. Since the big and rough spherulite which reaches the diameter of 20-150 microns at the time of crystallization of PFA is formed about the crystallinity of a polymer and a spherulite border area serves as a trench on a paint film or a moldings front face, the 2nd factor has an adverse effect on smooth nature. About this 2nd factor, examination is not made at all conventionally.

## [Problem(s) to be Solved by the Invention]

[0003] Since the object of this invention has the detailed spherulite which is excellent in a film plasticity and is formed at the time of crystallization, it is in offering the powder constituent of PFA which gives the paint film which was excellent in surface smooth nature with powder processing of powder coating, rotational casting, etc., and a moldings.

[0004]

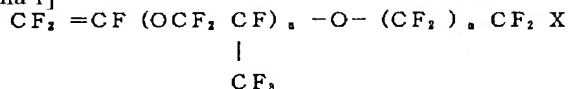
[Means for Solving the Problem] this invention persons find out that the surface smooth nature of a paint film or a rotational casting object formed from PFA powder is remarkably improvable, without making a spherulite detailed and moreover spoiling other properties of PFA by making PFA contain specific little polytetrafluoroethylene (PTFE), as a result of inquiring in order to attain the aforementioned object.

[0005] Namely, this invention The polytetrafluoroethylene particle and the heat of crystallization whose heat of crystallization is 50J/g or more contain at least one sort of polytetrafluoroethylene particles chosen from the colloid polytetrafluoroethylene particle of less than 50 J/g. They are the tetrafluoroethylene / perfluoro (alkoxy trifluoro ethylene) copolymer powder constituent which changes. The mean particle diameter of this powder constituent by 1-1000 microns and the formula  $\log_{10}$  of the following fluidity / no-load melting ] -- the ratio of a copolymer powder constituent [ in / the inside F of a F  $\geq 3.12 - 0.70 \log_{10} \eta$  type, and / in  $\eta / 372$  degrees C ] -- melt viscosity (poise) is expressed. [ the no-load melting fluidity of a copolymer powder constituent ] ] It is the fluororesin powder constituent for powder processing characterized by being satisfied.

[0006] In this invention, tetrafluoroethylene / fluoro alkoxy trifluoro ethylene copolymer (PFA) is crystalline copolymers with the fluoro alkoxy trifluoro ethylene expressed with tetrafluoroethylene, the following type (1), or a formula (2).

[0007]

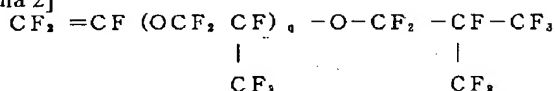
[Formula 1]



(For H, or F and n, the integer of 0-4 and m are [ X ] the integer of 0-7)

[0008]

[Formula 2]



(q is the integer of 0-3)

[0009] That whose fluoro alkoxy trifluoro ethylene content in PFA used for the powder constituent of this invention is 1 - 10 % of the weight is desirable. this copolymer -- again -- 372\*\*1 degree C -- setting -- 0.5 to 100x104 the ratio of the range of a poise -- the range desirable [ having melt viscosity ] and more desirable -- 0.5 to 50x104 It is a poise. a ratio -- melt viscosity -- 0.5x104 case it is lower than a poise -- the time of melting -- "-- by ", the moldings of uniform thickness is difficult to get, and the stress crack-proof nature of a moldings also gets worse. a ratio -- melt viscosity -- 100x104 When higher than a poise, a film plasticity falls and it is difficult to get in a uniform paint film and a uniform moldings. Although the powder of PFA used as the raw material of the constituent of this invention is obtained by which approaches, such as a \*\*\*\* polymerization, a solvent polymerization, and an emulsion polymerization, in order to acquire the PTFE particle which carries out a postscript, and the most uniform possible mixed state, as for the mixed front stirrup with a PTFE particle, it is desirable [ the mean particle diameter of raw material PFA powder ] to consider as 10 microns or less during mixing.

[0010] PTFE which carries out addition mixing at Above PFA is the denaturation PTFE containing modifiers, such as a homopolymer of tetrafluoroethylene or hexafluoropropylene (HFP) of less than 1% of the weight of a minute amount, fluoro alkoxy trifluoro ethylene, fluoro alkyl ethylene, and chlorotrifluoroethylene.

[0011] In this invention, even if it is the PTFE particle whose heat of crystallization is 50 or more J/g as these PTFE or the heat of crystallization is less than 50 J/g, if it is a colloid PTFE particle, it can be used. That is, PTFE which carries out addition combination requires that the polytetrafluoroethylene particle and (2) heat of crystallization whose (1) heat of crystallization is 50J/g or more should be at least one sort of polytetrafluoroethylene particles chosen from the colloid polytetrafluoroethylene particle of less than 50 J/g to PFA powder.

[0012] Above PTFE (1) can be obtained by the polymerization of TFE under existence of radiation irradiation decomposition and the pyrolysis of the amounts PTFE of macromolecules, such as "molding powder" and "fine powder", or a chain transfer agent etc. Although PTFE (1) usually comes to hand as powder with a mean particle diameter of 20 microns or less, mean particle diameter is not limited to this. Since such PTFE is low molecular weight, it can very be easy to crack it, and it can carry out pulverization easily by the mixing process with PFA powder, and can acquire the uniform mixed state with PFA. Above PTFE (2) has high molecular weight compared with PTFE (1). A colloid PTFE particle is a PTFE particle which has the mean particle diameter of 0.05-1 micron, and it can obtain according to an emulsion polymerization here. On the other hand, the object of this invention cannot be attained in PTFE by which the heat of crystallization is less than 50 J/g, and has the mean particle diameter of dozens of microns to hundreds of microns like the "molding powder" obtained, for example by the suspension polymerization.

[0013] The diameter of an average spherulite decreases rapidly by making PFA contain PTFE which satisfies said conditions. When crystallizing a constituent with 10-degree-C cooling rate for /from a melting condition as a content of PTFE, it is desirable to make 15 microns or less into the effective dose which can give the diameter of an average spherulite 10 microns or less preferably, and 0.01% of the weight or more of a content is usually preferably adopted 0.001% of the weight or more to the total quantity with PFA.

[0014] In order to raise the surface smooth nature of mold goods, it is desirable to make the diameter of an average spherulite as small as possible. Although the diameter of an average spherulite tends to decrease with the increment in a PTFE content, if a content becomes 1% of the weight or more, the diameter of an average spherulite will become almost fixed.

[0015] a ratio [ in / in the no-load melting fluidity F measured by the approach of carrying out a postscript in the powder constituent of this invention / 372 degrees C of a powder constituent ] -- it is required to satisfy the following formula connected with melt viscosity eta.

$\log 10 F \geq 3.12 - 0.70 \log 10 \eta$  [0016] No-load melting fluidity is difficult to get in a smooth surface paint film and a surface smooth moldings in the constituent with which are not satisfied of the above-mentioned formula. Reduce the no-load melting fluidity of a constituent, an excessive PTFE content tends to spoil surface smooth nature, and this inclination is remarkable in especially PTFE of the amount of macromolecules. Therefore, a PTFE content must be chosen within limits which satisfy the formula of the above [ no-load melting fluidity ]. Since it depends for the upper limit of such a PTFE content on the molecular weight of PTFE greatly, if the relation between the molecular weight of PTFE and the heat of crystallization with functionality is shown, in the amount PTFE of macromolecules which has the heat of crystallization of less than 50 J/g 25 or less % of the weight in the low molecular weight PTFE which has the heat of crystallization of 50 or more J/g, 0.1 or less % of the weight of a content will serve as a rule of thumb more preferably 0.2 or less % of the weight 1 or less % of the weight. In addition, since the inclination for a mechanical property to fall with 10% of the weight or more of a content in PTFE which has the heat of crystallization 50J [ /g ] or more also appears, 10 or less % of the weight of a content is more desirable.

[0017] There is especially no definition in the mixed approach with Above PFA and PTFE, and any approaches by which the uniform mixed state, such as the wet blending method with the dryblend method of PFA powder and PTFE powder, PFA dispersion liquid, PTFE powder, or PTFE dispersion liquid, is acquired can be used. Moreover, beforehand, distribute the particle of PTFE in the polymerization medium in the polymerization tank of PFA, the polymerization of PFA is made to start, and approaches, such as obtaining the PFA constituent containing PTFE, can also be taken.

[0018] Since the powder after mixing raises fine-particles properties, such as apparent specific gravity, it can carry out various kinds of processings by the well-known approach. It is the approach of grinding the approach (3) mixing powder ground after compressing mixed powder with the approach (JP,53-11296,B, JP,52-44576,B) (2) roll and press which spray (1) mixing powder or dispersion liquid as such an art into the ambient atmosphere heated more than the melting point of PFA after granulation or granulation under existence of a hydrophobic solvent or coexistence of a hydrophobic solvent and water. (4) After condensing the mixed aqueous dispersion liquid of PFA and PTFE, the approach of adding a hydrophobic solvent and pulverizing after granulation or granulation etc. can be mentioned.

[0019] In order to raise the collapsibility-proof of the particle of TFE system copolymer granulation powder to JP,62-260849,A, Although using the high fibrosis inclination of the "molding powder" of high PTFE of a fibrosis inclination and "fine powder", and adding these PTFE as a binder is proposed Since PTFE of less than 40 J/g which there is almost no fibrosis inclination and has a high fibrosis inclination is also used in a minute amount, there is no effectiveness of raising collapsibility-proof as a binder among PTFE used by this invention at PTFE of 40 or more J/g of heat of crystallization. Therefore, since it collapses, and pulverization is carried out and a fine-particles property tends to get worse, as for the powder corned by approaches, such as the above (3) and (4), it is desirable to carry out heat weld of the granulation powder at the temperature which does not exceed the melting point beyond the fusion initiation temperature of PFA, for example, 265-310 degrees C, in order to prevent this. Moreover, the powder particle obtained by grinding by (2) - (4) can also carry out heat weld of the powder after grinding at the same temperature in order to usually improve this by the infinite form, since apparent density gravity is low.

[0020] Furthermore, a polymer end group can also be stabilized by carrying out fluorine gassing of the powder before mixing, or the powder constituent after mixing by the approach of JP,62-104822,A or JP,2-163128,A in order to raise the thermal stability at the time of melting of a mixed powder constituent.

[0021] The powder constituent of this invention can contain various well-known thermostabilizers. As a thermostabilizer, although the powder (JP,5-112690,A) of an amine system antioxidant, an organic sulfur system compound (JP,55-9603,A), tin or zinc powder (JP,55-50066,B), a phenolic antioxidant (JP,55-38802,A), and polyphenylene sulfide (PPS) etc. can be illustrated, in the point which is excellent in chemical resistance and does not have the problem of an effluent, PPS powder is desirable as a thermostabilizer.

[0022] The powder constituent of this invention can also contain various kinds of fillers depending on an application. As a filler, metal powder, a metal fiber, carbon black, carbon fiber, silicon carbide, a glass fiber, a glass bead, a glass flake, graphite, heat resistant resin, for example, polyphenylene sulfide, polyimide, polyamidoimide, polyether sulfone, a polyether ether ketone, aromatic polyamide, etc. can be illustrated. In order to attain the object of this invention, as for a bulking agent, it is desirable to have the shape of impalpable powder no adverse effect is [ shape ] in surface smooth nature.

[0023] 100-1000 microns of mean particle diameter which the powder constituent for powder processing of this invention obtained by the above has the mean particle diameter of 1-1000 microns, and was suitable for powder molding, such as rotational casting and revolution lining, are 150-500 microns preferably, and the mean particle diameter suitable for powder coating is 1-150 microns.

[0024]

[Effect of the Invention] It comes out of the powder constituent of this invention to process it according to the same processing conditions as the conventional PFA powder for powder processing. The front face of works, such as lining or a container by which coating was carried out, a pipe, and a joint, is excellent in smooth nature with the container obtained by rotational casting, a pipe, revolution lining, or powder coating compared with the front face of the work obtained from the conventional PFA powder. Therefore, the dust particle adhering to a work front face is removable by short-time washing. Since PTFE used as an additive has thermal resistance and chemical resistance equivalent to PFA, the physical properties on the front face of a work are also excellent. Especially the work obtained from the constituent which does not contain the component eluted with drug solutions, such as a metal, as a thermostabilizer or a filler among the constituents of this invention fits the facility for dealing with the high grade drug solution used by the semi-conductor production process which dislikes mixing of a foreign matter.

[0025]

[Example] An example and the example of a comparison are shown below, and this invention is concretely explained to it. In addition, the measurement of the class of raw materials PFA and PTFE used in the example and the example of a comparison and the physical properties of the obtained constituent is as follows.

[0026] (A) Raw material fluoro resin (1) The PFA following four sorts of tetrafluoroethylene / perfluoro (propyl vinyl ether) (PPVE) copolymer aqueosity dispersion liquid were used.

[0027]

[A table 1]

PFA 種類	a	b	c	d
平均粒径 (ミクロン)	0.2	0.2	0.2	0.2
PPVE 含有量 (重量%)	3.4	3.5	3.5	3.1
融解温度 (°C)	308	307	307	308
比溶解粘度 ( $\times 10^4$ ポイズ)	4.0	3.8	13	33

[0028] (2) The PTFE following seven sorts of PTFE powder and aqueosity dispersion liquid were used.

[0029]

[A table 2]



PTFE 粉末						PTFE 水性分散液	
PTFE の種類	A	B	C	D	E	F	G
変性剤の種類 含有量 wt %	なし	PPVE 0.1	HFP 0.1	なし	なし	なし	HFP 0.3
平均粒径 (ミクロン)	5	8	2	6	29	0.20	0.1
T <sub>m1</sub> °C	332	331	322	326	345		
T <sub>m2</sub> °C	328	328	324	328	328		
T <sub>c</sub> °C	316	313	312	308	314	314	306
H <sub>c</sub> J/g	58	53	59	67	23	34	47

[0030] (B) Physical-properties measuring method (1) The PPVE content measuring method in PFA: After compressing Sample PFA at 350 degrees C, it asked for the extinction quotient by the following formula from the infrared absorption spectrum (nitrogen-gas-atmosphere mind) of a film with a thickness of about 50 microns obtained by carrying out water cooling, and the PPVE content of a sample was calculated using the calibration curve beforehand acquired with the standard film of PPVE content

$$\text{吸光度比} = \frac{\text{吸光度 (波長 10.07 ミクロン)}}{\text{吸光度 (波長 4.25 ミクロン)}}$$

known. \*\*

吸光度 (波長 4.25 ミクロン)

[0031] (2) The melting out temperature, the crystallization temperature, and the DSC by heat-of-crystallization PerkinElmer, Inc. 7 mold of PTFE were used. After carrying out weighing capacity of the 5mg of the samples, putting into the aluminum pan of dedication and carrying out crimp by the crimper of dedication, it contains on a DSC body and temperature up is started. Temperature up was carried out by part for 10-degree-C/from 200 degrees C to 380 degrees C, and fusion peak temperature was searched for as a melting out temperature (T<sub>m1</sub>:degree C) from the melting curve obtained at this time. After holding a sample for 1 minute at 380 degrees C, the temperature was lowered by part for 10-degree-C/to 200 degrees C, and crystallization peak temperature was searched for as crystallization temperature (T<sub>c</sub>:degree C) from the crystallization curve obtained at this time. According to the conventional method, it asked for the heat of crystallization (H<sub>c</sub>:J/g) from the peak area which connects the point that a curve separates from the base line before and behind a crystallization peak, and the point which returns to the base line in a straight line, and is defined. After holding a sample for 1 minute at 200 degrees C, again, temperature up was carried out by part for 10-degree-C/to 380 degrees C, and fusion peak temperature was searched for as a melting out temperature (T<sub>m2</sub>, \*\*) from the melting curve obtained at this time.

[0032] (3) powder with a powdered mean-particle-diameter mean particle diameter of 100 microns or more -- a JIS standard sieve and electromagnetism -- the shaking screen machine (FRITSH ANALYSETTE) was used, and particle size distribution were measured by the dry type screen method in the amount of samples of 50g, and it asked for mean particle diameter. About powder with a mean particle diameter of 100 microns or less, particle size distribution were measured using the Shimadzu centrifugation type particle-size-distribution measuring device (SA-CP4L), and it asked for mean particle diameter.

[0033] (4) According to the approach of a dispersion-liquid colloid particle given in mean-particle-diameter U.S. Pat. No. 3,391,099, whenever [ light transmission / of the dilution dispersion liquid in the wavelength of 0.546 microns ] was measured, and it asked for mean particle diameter based on correlation of the mean particle diameter defined beforehand and whenever light transmission ].

[0034] (5) It was put on the slide glass, having used as the sample the disc-like intercept with a thickness of about 0.2mm which sliced the test piece after the diameter no-load melting fluidity measurement of an average spherulite in the thickness direction, and was obtained, and was attached in the METORA FP82HT mold hot stage. Temperature up is carried out by part for 10-degree-C/to 360 degrees C, and a sample is dissolved, and after holding for 3 minutes at 360 degrees C, it was made to lower the temperature and recrystallize by part for 10-degree-C/to 200 degrees C. The sample front face was observed by the optical microscope scale factor 100 and 400 times, having removed the slide glass which carried the sample from the hot stage, and checking spherulite structure by polarization, after sample section temperature amounted to 200 degrees C. The diameter of 200 continuous spherulites observed on a sample front face was measured, and the average was made into the diameter of an average spherulite. In addition, since the spherulite was observed as a distorted polygon by the collision with the spherulite which adjoined and grew, the diameter of a major axis was made into the diameter. Moreover, the diameter of an average spherulite used together the scanning electron microscope (3000 times and 5000 times) about the sample 5 microns or less, and measured the diameter of a spherulite.

[0035] (6) It calcinated at 360 degrees C for 1 hour all over the circulating reactor of the post heating style which placed the diameter of 40mm, and the circular aluminum frame of height \*\* of 10mm on the mild steel plate with a thickness of 1mm ground with surface roughness #600 sandpaper, and was filled up with about 5g of powder constituents into it, it took out from the furnace, and cooled radiationally to the room temperature, and the test piece with a thickness of about 2mm was obtained. The average of roughness height was measured about the front face of this test piece using the scanning laser microscope (Lasertec ILM21 mold). In addition, in the example 22 and the example 11 of a comparison, the average of roughness height was measured [ front face / of the electrostatic-coating film ] about the revolution lining side by the example 23 and the example 12 of a

comparison.

[0036] (7) About 5 kgf/cm<sup>2</sup> after being filled up with tensile strength and an elongation sample into the metal mold heated by 350 degrees C on a hotpress and heating it for 20 minutes It pressurizes for about 1 minute by the pressure, subsequently to the press top of a room temperature metal mold is moved, and they are about 30 kgf/cm<sup>2</sup>. It pressurizes, and it is left for 20 minutes and cools. Thus, from the sheet with a thickness of about 1.5mm created, the test piece of five sheets was cut down according to ASTM D 1457-83, the tensile test was performed by part for 50mm/in initial grip spacing of 22.2mm, and tension rate, and the reinforcement and elongation (average of five test pieces) at the time of fracture were searched for.

[0037] (8) a ratio -- the melt indexer made from a melt viscosity Oriental energy machine was used, after filling up with the 5g powder sample the cylinder with a bore of 9.53mm held at 372 degrees C  $\pm$  1 degree C and holding it for 5 minutes, it extruded through the orifice with a bore [ of 2.1mm ], and a die length of 8mm under the 5kg load (a piston and weight), and the knockout rate at this time (a part for g/) was found. a ratio -- melt viscosity was computed by the following formula.

a ratio -- melt viscosity  $\eta$  (poise) =  $53150 / \text{extrusion rate (a part for g)}$

[0038] (9) No-load melting fluidity (F)

The disc-like test piece of diameter 25(D0) mm pierced from 2mm sheet in thickness which carried out melting compression molding and obtained the powder non-constituent at 370 degrees C, and thickness 2(t) mm is placed on a mild steel plate with a thickness of 1mm ground with the sandpaper of #600, and after heating for 30 minutes at 310 degrees C all over a hot blast circulating reactor, it heats at 360 degrees C for further 1 hour. Subsequently, the mild steel plate which carried the test piece is cooled radiationally from a furnace to an ejection room temperature. It fuses, the diameter (D1) of the spreading test piece is measured, and the no-load melting fluidity F is computed by the degree type.

$F = (D1 - D0) / 2t$  [0039] (10) Marginal melting fluidity (f)

a ratio [ in / by the following formula / 372 degrees C of a powder constituent ] -- the f value and the above (9) which computed from melt viscosity  $\eta$  and were obtained Size with the F value of the obtained location survey was compared. (this invention constituent  $F \geq f$ )

$\log 10 f = 3.12 - 0.70 \log 10 \eta$  [0040] examples 1-4, the [examples 1-2 of comparison] mean particle diameter of 0.2 microns, the PPVE content of 3.4 % of the weight, the melting out temperature of 308 degrees C, and a ratio -- melt viscosity  $4.0 \times 10^4$  while agitating to the aqueous dispersion liquid of PFA of a poise -- a nitric acid -- subsequently trichlorofluoroethane was added, the end of agglomerated powder was obtained, and this was dried at 150 degrees C for 10 hours. In this way, it is 1 weight section and a thermostabilizer, respectively about PTFE powder A-E shown in the obtained desiccation powder 99 weight section and a table 2. After supplying the PPS ("Ryton" made from TOSOH SASUTIRU V-1 grinding article) powder 1 weight section, and the pure-water 15 weight section to the Henschel mixer (FM10 made from Mitsui Miike chemically-modified opportunity B mold) and mixing for 10 minutes by 3000rpm, the trichlorofluoroethane 50 weight section was added small quantity every, it agitated for 1 minute by 1000rpm, and granulation powder was obtained. Subsequently, after heat-treating this at 300 degrees C for 10 hours, it classified with the screen of 1000 microns of openings, and the powder constituent of a passing sieve was made into the sample. The property of the test piece obtained from this powder constituent and it is shown in a table 3 with the result of the example of a comparison which does not add PTFE powder. The test piece obtained from the powder constituent which added a PTFE additive-free thing and small PTFE of the heat of crystallization was inferior in surface smooth nature. In addition, the mean particle diameter of the powder which supplied only the desiccation agglomerated powder end of above PFA to the Henschel mixer, processed for 10 minutes and was obtained by 3000rpm was 8 microns.

[0041] examples 5-13, the [examples 3-5 of comparison] mean particle diameter of 0.2 microns, the PPVE content of 3.5 % of the weight, the melting out temperature of 307 degrees C, and a ratio -- melt viscosity  $3.8 \times 10^4$  The powder constituent was obtained like the example 1 with the PTFE addition shown in a table 4 and a table 5 using the aqueous dispersion liquid of PFA of a poise, and the PTFE powder A. The property of a powder constituent and a test piece is shown in a table 4 and a table 5. the constituent which added PTFE to the large quantity -- a ratio -- the surface smooth nature of the test piece which it became difficult to fabricate a test piece and was obtained with the relative low therefore no-load melting fluidity to melt viscosity worsens.

[0042] an example 14, the [example 6 of comparison] mean particle diameter of 0.2 microns, the PPVE content of 3.5 % of the weight, the melting out temperature of 307 degrees C, and a ratio -- melt viscosity  $13 \times 10^4$  The aqueous dispersion liquid of PFA of a poise and the PTFE powder A were used, and the powder constituent was obtained like the example 1 so that the rate of PTFE in a pitch might become 0.5 % of the weight. The property of the test piece obtained from this powder constituent and it is shown in a table 6 with the result of the example of a comparison which does not add PTFE powder.

[0043] an example 15, the [example 7 of comparison] mean particle diameter of 0.2 microns, the PPVE content of 3.1 % of the weight, the melting out temperature of 308 degrees C, and a ratio -- melt viscosity  $33 \times 10^4$  The aqueous dispersion liquid of PFA of a poise and the PTFE powder A were used, and the powder constituent was obtained like the example 1 so that the rate of PTFE in a pitch might become 0.5 % of the weight. The property of the test piece obtained from this powder constituent and it is shown in a table 6 with the result of the example of a comparison which does not add PTFE powder.

[0044] After adding to the aqueous dispersion liquid of PFA which used the aqueous dispersion liquid F of PTFE of the mean particle diameter of 0.2 microns, and 34J/g of heat of crystallization which are the raw material of examples 16-20 and the [examples 8-10 of comparison] marketing "fine powder" in the example 1 so that the rate of PTFE in a pitch may become 0.001 - 1 % of the weight, and adding PPS powder at 1% of the weight of a rate to a pitch to them further, while agitating The nitric acid was added, the emulsion was destroyed, subsequently trichlorofluoroethane was added and churning granulation was carried out. Thus, after rinsing the obtained granulation powder and carrying out desiccation heat weld at 300 degrees C for 10 hours, the

powder constituent was obtained by classifying with the screen of 1000 microns of openings. The property of a powder constituent and a test piece is shown in a table 7 with the result of the example of a comparison which did not add PTFE powder for the same actuation, but was carried out.

[0045] To the [example 21] mean particle diameter of 0.13 microns, and the aqueous dispersion liquid of PFA which used the aqueous dispersion liquid G of PTFE of heat-of-crystallization 47 J/g in the example 1, it added so that the rate of PTFE in a pitch might become 1 % of the weight, and the powder constituent was obtained like the example 16 to them. The property of a powder constituent and a test piece is shown in a table 8.

[0046] [An example 22, the example 11 of a comparison] (surface roughness test of the electrostatic-coating film)  
The 99.5 weight sections and the PTFE powder A0.5 weight section were supplied to the Henschel mixer in the agglomerated powder end of PFA dried at 150 degrees C by the example 1, and granulation powder was obtained like the example 1. After heat-treating this granulation powder at 290 degrees C for 4 hours, it ground by rotational frequency 10000rpm using the ultracentrifuge mill (ZM made from RETCH- 1). The screen and the powder constituent of a passing sieve were obtained by 150 microns of backward openings which heat-treated this end of a pulverized powder at 300 degrees C for 6 hours. Electrostatic blasting of this powder constituent was carried out on the aluminum plate, it calcinated for 30 minutes at 360 degrees C, and the paint film with a thickness of about 80 microns was obtained. The property of a powder constituent and the surface roughness of a paint film are shown in a table 9 with the result of the example of a comparison which did not add PTFE powder for the same actuation, but was carried out.

[0047] [An example 23, the example 12 of a comparison] (surface roughness test of a revolution lining side)  
The powder constituent was obtained like the example 14 except not adding PPS. Revolution lining of a steel pipe inner surface was carried out according to the following conditions using this powder constituent. The same actuation is shown in a table 10 with the result of the example of a comparison which did not add PTFE powder for the property of a powder constituent, and the surface roughness of a lining side, but was carried out.

[0048] Metal mold: 3B black steel pipe (the bore of 80mm, die length of 150mm)

# 60 alumina sandblasting processing resin input: 200g (thickness of about 2mm)

Making machine: Product made from Tamagawa Machine Biaxial 100L rotational casting machine revolution 3.5rpm Rotation 5.0rpm baking conditions: 300->320 degrees C 320 degrees C of 5-minute temperature up 30 minutes [ of maintenance ] 320->360 degrees C 360 degrees C of 5-minute temperature up Maintenance 180-minute air cooling 20 minutes [0049]

[A table 3]

		比較例		実施例				比較例
番 号		1	1	2	3	4		2
PFAの種類		a (比熔融粘度 $4.0 \times 10^4$ ポイズ)						
PTFEの種類		無添加	A	B	C	D	E	
粉	PTFE含有量 wt%	0	1	1	1	1	1	
	PPS含有量 wt%	1	1	1	1	1	1	
末	平均粒径 ミクロン	375	405	400	400	435	390	
	比熔融粘度 $\times 10^4$ ポイズ	4.0	4.1	3.9	5.9	4.0	4.4	
組	限界熔融流動度 f (計算値)	0.8	0.8	0.8	0.6	0.8	0.7	
	無荷重熔融流動度 F (実測値)	1.7	1.7	1.7	1.6	1.7	1.7	
試	平均球粒径 ミクロン	65	3	5	6	8	45	
	平均粗さ ミクロン	0.5	0.1	0.1	0.1	0.1	0.7	

[0050]

[A table 4]

		比較例		実施例			
番 号		3	5	6	7	8	9
PFAの種類		b (比溶融粘度 $3.8 \times 10^4$ ポイズ)					
PTFEの種類		A	A	A	A	A	A
粉末組成物試験片	PTFE含有量 wt%	0	0.001	0.01	0.1	0.5	1
	PPS含有量 wt%	1	1	1	1	1	1
	平均粒径 ミクロン	385	395	410	385	370	370
	比溶融粘度	3.8	3.8	3.8	3.8	3.8	3.9
	限界溶融流動度 (計算値)	0.8	0.8	0.8	0.8	0.8	0.8
	無荷重溶融流動度 (実測値)	1.8	1.8	1.8	1.8	1.8	1.7
	平均球晶径 ミクロン	40	15	7	5	4	4
	平均粗さ ミクロン	0.4	0.2	0.1	0.1	0.1	0.1
試験片	引張強度 $\text{Kgf/cm}^2$	320			290		280
	引張伸び %	420			390		400

[0051]

[A table 5]

		実施例				比較例	
番 号		10	11	12	13	4	5
PFAの種類		b (比溶融粘度 $3.8 \times 10^4$ ポイズ)					
PTFEの種類		粉末 A ( $T_c = 316^\circ\text{C}$ , $H_c = 58\text{J/g}$ )					
粉末組成物試験片	PTFE含有量 wt%	2	5	10	20	30	50
	PPS含有量 wt%	1	1	1	1	1	1
	平均粒径 ミクロン	390	420	400	370	400	380
	比溶融粘度	3.9	4.4	4.8	5.9	11	27
	限界溶融流動度 (計算値)	0.8	0.7	0.7	0.6	0.4	0.2
	無荷重溶融流動度 (実測値)	1.6	1.3	1.1	0.7	0.1	0.0
	平均球晶径 ミクロン	3	3	3	3	3	3
	平均粗さ ミクロン	0.1	0.1	0.1	0.2	0.5	*
試験片	引張強度 $\text{Kgf/cm}^2$	270	240	220	200	180	150
	引張伸び %	360	360	240	160	100	20

\* Carry out crack initiation and it is film formation impossible. [0052]

[A table 6]

		比較例		実施例	
番 号		6	14	7	15
PFAの種類		c (比溶融粘度 $13 \times 10^4$ ポイズ)		d (比溶融粘度 $33 \times 10^4$ ポイズ)	
PTFEの種類		無添加	A	無添加	A
粉末組成物試験片	PTFE含有量 wt%	0	0.5	0	0.5
	PPS含有量 wt%	1	1	1	1
	平均粒径 ミクロン	221	228	390	395
	比溶融粘度 $\times 10^4$ ポイズ	13	13	33	33
	限界溶融流動度 (計算値)	0.3	0.3	0.2	0.2
	無荷重溶融流動度 (実測値)	1.2	1.2	0.6	0.6
	平均球晶径 ミクロン	85	3	60	4
	平均粗さ ミクロン	0.5	0.1	0.4	0.1

[0053]

[A table 7]

		比較例	実 施 例						比 較 例
番 号		8	16	17	18	19	20	9	10
PFAの種類		a (比溶融粘度 $4.0 \times 10^4$ ポイズ)							
PTFEの種類		無添加	水性分散液F						
粉 末 組 成 物	PTFE含有量 wt%	0	0.001	0.005	0.01	0.05	0.1	0.5	1
	PPS含有量 wt%	1	1	1	1	1	1	1	1
	平均粒径 ミクロン	405	410	390	365	380	405	395	390
	比溶融粘度 $\times 10$ ポイズ	4.0	4.0	4.0	4.1	4.2	4.6	5.1	6.8
	限界溶融 流動度 (計算値)	0.8	0.8	0.8	0.8	0.8	0.7	0.7	0.5
	無荷重溶融 流動度 (実測値)	1.7	1.7	1.7	1.6	1.4	1.2	0.5	0.1
試 験 片	平均球晶径 ミクロン	65	13	7	5	4	3	2	2
	平均粗さ ミクロン	0.5	0.2	0.1	0.1	0.1	0.1	0.3	0.6

[0054]

[A table 8]

		実 施 例
番 号		21
PFAの種類		a ( $4.0 \times 10^4$ ポイズ)
PTFEの種類		水性分散液G
粉 末 組 成 物	PTFE含有量 wt%	1
	PPS含有量 wt%	1
	平均粒径ミクロン	385
	比溶融粘度 $\times 10$ ポイズ	5.2
	限界溶融流動度 (計算値)	0.7
無荷重溶融流動度 (実測値)		0.8
試 験 片	平均球晶径ミクロン	5
	平均粗さ ミクロン	0.2

[0055]

[A table 9]

		比較例	実施例
番 号		11	22
PFAの種類		a ( $4.0 \times 10^4$ ボイズ)	
PTFEの種類		無添加	粉末A
粉末組成物	PTFE含有量 wt%	0	0.5
	PFS 含有量 wt%	0	0
	平均粒径 ミクロン	39	36
	比溶解粘度 $\times 10^4$ ボイズ	4.0	4.0
	限界溶解流動度 (計算値)	0.8	0.8
	無荷重溶解流動度 (実測値)	1.8	1.8
試験片	平均球晶径 ミクロン	65	4
	平均粗さ ミクロン (塗膜面)	0.4	0.1

[0056]

[A table 10]

		比較例	実施例
番 号		12	23
PFAの種類		c ( $13 \times 10^4$ ボイズ)	
PTFEの種類		無添加	PTFE粉末A
粉末組成物	PTFE含有量 wt%	0	0.5
	PFS 含有量 wt%	0	0
	平均粒径 ミクロン	378	402
	比溶解粘度 $\times 10^4$ ボイズ	13	13
	限界溶解流動度 (計算値)	0.3	0.3
	無荷重溶解流動度 (実測値)	1.2	1.2
試験片	平均球晶径 ミクロン	85	4
	平均粗さ ミクロン (ライニング面)	0.6	0.1

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[0012] Above PTFE (1) can be obtained by the polymerization of TFE under existence of radiation irradiation decomposition and the pyrolysis of the amounts PTFE of macromolecules, such as "molding powder" and "fine powder", or a chain transfer agent etc. Although PTFE (1) usually comes to hand as powder with a mean particle diameter of 20 microns or less, mean particle diameter is not limited to this. Since such PTFE is low molecular weight, it can very be easy to crack it, and it can carry out pulverization

easily by the mixing process with PFA powder, and can acquire the uniform mixed state with PFA. Above PTFE (2) has high molecular weight compared with PTFE (1). A colloid PTFE particle is a PTFE particle which has the mean particle diameter of 0.05-1 micron, and it can obtain according to an emulsion polymerization here. On the other hand, the object of this invention cannot be attained in PTFE by which the heat of crystallization is less than 50 J/g, and has the mean particle diameter of dozens of microns to hundreds of microns like the "molding powder" obtained, for example by the suspension polymerization.

[0013] The diameter of an average spherulite decreases rapidly by making PFA contain PTFE which satisfies said conditions. When crystallizing a constituent with 10-degree-C cooling rate for /from a melting condition as a content of PTFE, it is desirable to make 15 microns or less into the effective dose which can give the diameter of an average spherulite 10 microns or less preferably, and 0.01% of the weight or more of a content is usually preferably adopted 0.001% of the weight or more to the total quantity with PFA.

[0014] In order to raise the surface smooth nature of mold goods, it is desirable to make the diameter of an average spherulite as small as possible. Although the diameter of an average spherulite tends to decrease with the increment in a PTFE content, if a content becomes 1% of the weight or more, the diameter of an average spherulite will become almost fixed.

[0015] a ratio [ in / in the no-load melting fluidity F measured by the approach of carrying out a postscript in the powder constituent of this invention / 372 degrees C of a powder constituent ] -- it is required to satisfy the following formula connected with melt viscosity etc.

$\log 10F \geq 3.12 - 0.70 \log 10\eta$  [0016] No-load melting fluidity is difficult to get in a smooth surface paint film and a surface smooth moldings in the constituent with which are not satisfied of the above-mentioned formula. Reduce the no-load melting fluidity of a constituent, an excessive PTFE content tends to spoil surface smooth nature, and this inclination is remarkable in especially PTFE of the amount of macromolecules. Therefore, a PTFE content must be chosen within limits which satisfy the formula of the above [ no-load melting fluidity ]. Since it depends for the upper limit of such a PTFE content on the molecular weight of PTFE greatly, if the relation between the molecular weight of PTFE and the heat of crystallization with functionality is shown, in the amount PTFE of macromolecules which has the heat of crystallization of less than 50 J/g 25 or less % of the weight in the low molecular weight PTFE which has the heat of crystallization of 50 or more J/g, 0.1 or less % of the weight of a content will serve as a rule of thumb more preferably 0.2 or less % of the weight 1 or less % of the weight. In addition, since the inclination for a mechanical property to fall with 10% of the weight or more of a content in PTFE which has the heat of crystallization 50J [ /g ] or more also appears, 10 or less % of the weight of a content is more desirable.

[0017] There is especially no definition in the mixed approach with Above PFA and PTFE, and any approaches by which the uniform mixed state, such as the wet blending method with the dryblend method of PFA powder and PTFE powder, PFA dispersion liquid, PTFE powder, or PTFE dispersion liquid, is acquired can be used. Moreover, beforehand, distribute the particle of PTFE in the polymerization medium in the polymerization tank of PFA, the polymerization of PFA is made to start, and approaches, such as obtaining the PFA constituent containing PTFE, can also be taken.

[0018] Since the powder after mixing raises fine-particles properties, such as apparent specific gravity, it can carry out various kinds of processings by the well-known approach. It is the approach of grinding the approach (3) mixing powder ground after compressing mixed powder with the approach (JP,53-11296,B, JP,52-44576,B) (2) roll and press which spray (1) mixing powder or dispersion liquid as such an art into the ambient atmosphere heated more than the melting point of PFA after granulation or granulation under existence of a hydrophobic solvent or coexistence of a hydrophobic solvent and water. (4) After condensing the mixed aqueous dispersion liquid of PFA and PTFE, the approach of adding a hydrophobic solvent and pulverizing after granulation or granulation etc. can be mentioned.

[0019] In order to raise the collapsibility-proof of the particle of TFE system copolymer granulation powder to JP,62-260849,A, Although using the high fibrosis inclination of the "molding powder" of high PTFE of a fibrosis inclination and "fine powder", and adding these PTFE as a binder is proposed Since PTFE of less than 40 J/g which there is almost no fibrosis inclination and has a high fibrosis inclination is also used in a minute amount, there is no effectiveness of raising collapsibility-proof as a binder among PTFE used by this invention at PTFE of 40 or more J/g of heat of crystallization. Therefore, since it collapses, and pulverization is carried out and a fine-particles property tends to get worse, as for the powder corned by approaches, such as the above (3) and (4), it is desirable to carry out heat weld of the granulation powder at the temperature which does not exceed the melting point beyond the fusion initiation temperature of PFA, for example, 265-310 degrees C, in order to prevent this. Moreover, the powder particle obtained by grinding by (2) - (4) can also carry out heat weld of the powder after grinding at the same temperature in order to usually improve this by the infinite form, since apparent density gravity is low.

[0020] Furthermore, a polymer end group can also be stabilized by carrying out fluorine gassing of the powder before mixing, or the powder constituent after mixing by the approach of JP,62-104822,A or JP,2-163128,A in order to raise the thermal stability at the time of melting of a mixed powder constituent.

[0021] The powder constituent of this invention can contain various well-known thermostabilizers. As a thermostabilizer, although the powder (JP,5-112690,A) of an amine system antioxidant, an organic sulfur system compound (JP,55-9603,A), tin or zinc powder (JP,55-50066,B), a phenolic antioxidant (JP,55-38802,A), and polyphenylene sulfide (PPS) etc. can be illustrated, in the point which is excellent in chemical resistance and does not have the problem of an effluent, PPS powder is desirable as a thermostabilizer.

[0022] The powder constituent of this invention can also contain various kinds of fillers depending on an application. As a filler, metal powder, a metal fiber, carbon black, carbon fiber, silicon carbide, a glass fiber, a glass bead, a glass flake, graphite, heat resistant resin, for example, polyphenylene sulfide, polyimide, polyamidoimide, polyether sulfone, a polyether ether ketone, aromatic polyamide, etc. can be illustrated. In order to attain the object of this invention, as for a bulking agent, it is desirable to



have the shape of impalpable powder no adverse effect is [ shape ] in surface smooth nature.

[0023] 100-1000 microns of mean particle diameter which the powder constituent for powder processing of this invention obtained by the above has the mean particle diameter of 1-1000 microns, and was suitable for powder molding, such as rotational casting and revolution lining, are 150-500 microns preferably, and the mean particle diameter suitable for powder coating is 1-150 microns.

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## EXAMPLE

[Example] An example and the example of a comparison are shown below, and this invention is concretely explained to it. In addition, the measurement of the class of raw materials PFA and PTFE used in the example and the example of a comparison and the physical properties of the obtained constituent is as follows.

[0026] (A) Raw material fluoro resin (1) The PFA following four sorts of tetrafluoroethylene / perfluoro (propyl vinyl ether) (PPVE) copolymer aqueous dispersion liquid were used.

[0027]

[A table 1]

PFA 種類	a	b	c	d
平均粒径 (ミクロン)	0.2	0.2	0.2	0.2
PPVE 含有量 (重量%)	3.4	3.5	3.5	3.1
融解温度 (°C)	308	307	307	308
比溶液粘度 ( $\times 10^4$ ポイズ)	4.0	3.8	13	33

[0028] (2) The PTFE following seven sorts of PTFE powder and aqueous dispersion liquid were used.

[0029]

[A table 2]

PTFE 粉末						PTFE 水性分散液	
PTFE の種類	A	B	C	D	E	F	G
変性剤の種類 含有量 wt%	なし	PPVE 0.1	HFP 0.1	なし	なし	なし	HFP 0.3
平均粒径 (ミクロン)	5	8	2	6	29	0.20	0.1
T <sub>m1</sub> °C	332	331	322	326	345		
T <sub>m2</sub> °C	328	328	324	328	328		
T <sub>c</sub> °C	316	313	312	308	314	314	306
H <sub>c</sub> J/g	58	53	59	67	23	34	47

[0030] (B) Physical-properties measuring method (1) The PPVE content measuring method in PFA: After compressing Sample PFA at 350 degrees C, it asked for the extinction quotient by the following formula from the infrared absorption spectrum (nitrogen-gas-atmosphere mind) of a film with a thickness of about 50 microns obtained by carrying out water cooling, and the PPVE content of a sample was calculated using the calibration curve beforehand acquired with the standard film of PPVE content

$$\text{吸光度比} = \frac{\text{吸光度 (波長 10.07 ミクロン)}}{\text{吸光度 (波長 4.25 ミクロン)}}$$

known. \*\*

吸光度 (波長 4.25 ミクロン)

[0031] (2) The melting out temperature, the crystallization temperature, and the DSC by heat-of-crystallization PerkinElmer, Inc. 7 mold of PTFE were used. After carrying out weighing capacity of the 5mg of the samples, putting into the aluminum pan of dedication and carrying out crimp by the crimper of dedication, it contains on a DSC body and temperature up is started. Temperature up was carried out by part for 10-degree-C from 200 degrees C to 380 degrees C, and fusion peak temperature was searched for as a melting out temperature (T<sub>m1</sub>:degree C) from the melting curve obtained at this time. After holding a sample for 1 minute at 380 degrees C, the temperature was lowered by part for 10-degree-C to 200 degrees C, and crystallization peak temperature was searched for as crystallization temperature (T<sub>c</sub>:degree C) from the crystallization curve obtained at this time. According to the conventional method, it asked for the heat of crystallization (H<sub>c</sub>:J/g) from the peak area which connects the point that a curve separates from the base line before and behind a crystallization peak, and the point which returns to the base line in a straight line, and is defined. After holding a sample for 1 minute at 200 degrees C, again, temperature up was carried out by part

for 10-degree-C/to 380 degrees C, and fusion peak temperature was searched for as a melting out temperature ( $T_{m2}$ , \*\*) from the melting curve obtained at this time.

[0032] (3) powder with a powdered mean-particle-diameter mean particle diameter of 100 microns or more -- a JIS standard sieve and electromagnetism -- the shaking screen machine (FRITSH ANALYSETTE) was used, and particle size distribution were measured by the dry type screen method in the amount of samples of 50g, and it asked for mean particle diameter. About powder with a mean particle diameter of 100 microns or less, particle size distribution were measured using the Shimazu centrifugation type particle-size-distribution measuring device (SA-CP4L), and it asked for mean particle diameter.

[0033] (4) According to the approach of a dispersion-liquid colloid particle given in mean-particle-diameter U.S. Pat. No. 3,391,099, whenever [ light transmission / of the dilution dispersion liquid in the wavelength of 0.546 microns ] was measured, and it asked for mean particle diameter based on correlation of the mean particle diameter defined beforehand and whenever light transmission ].

[0034] (5) It was put on the slide glass, having used as the sample the disc-like intercept with a thickness of about 0.2mm which sliced the test piece after the diameter no-load melting fluidity measurement of an average spherulite in the thickness direction, and was obtained, and was attached in the METORA FP82HT mold hot stage. Temperature up is carried out by part for 10-degree-C/to 360 degrees C, and a sample is dissolved, and after holding for 3 minutes at 360 degrees C, it was made to lower the temperature and recrystallize by part for 10-degree-C/to 200 degrees C. The sample front face was observed by the optical microscope scale factor 100 and 400 times, having removed the slide glass which carried the sample from the hot stage, and checking spherulite structure by polarization, after sample section temperature amounted to 200 degrees C. The diameter of 200 continuous spherulites observed on a sample front face was measured, and the average was made into the diameter of an average spherulite. In addition, since the spherulite was observed as a distorted polygon by the collision with the spherulite which adjoined and grew, the diameter of a major axis was made into the diameter. Moreover, the diameter of an average spherulite used together the scanning electron microscope (3000 times and 5000 times) about the sample 5 microns or less, and measured the diameter of a spherulite.

[0035] (6) It calcinated at 360 degrees C for 1 hour all over the circulating reactor of the post heating style which placed the diameter of 40mm, and the circular aluminum frame of height \*\* of 10mm on the mild steel plate with a thickness of 1mm ground with surface roughness #600 sandpaper, and was filled up with about 5g of powder constituents into it, it took out from the furnace, and cooled radiationally to the room temperature, and the test piece with a thickness of about 2mm was obtained. The average of roughness height was measured about the front face of this test piece using the scanning laser microscope (Lasertec 1LM21 mold). In addition, in the example 22 and the example 11 of a comparison, the average of roughness height was measured [ front face / of the electrostatic-coating film ] about the revolution lining side by the example 23 and the example 12 of a comparison.

[0036] (7) About 5 kgf/cm<sup>2</sup> after being filled up with tensile strength and an elongation sample into the metal mold heated by 350 degrees C on a hotpress and heating it for 20 minutes It pressurizes for about 1 minute by the pressure, subsequently to the press top of a room temperature metal mold is moved, and they are about 30 kgf/cm<sup>2</sup>. It pressurizes, and it is left for 20 minutes and cools. Thus, from the sheet with a thickness of about 1.5mm created, the test piece of five sheets was cut down according to ASTM D 1457-83, the tensile test was performed by part for 50mm/in initial grip spacing of 22.2mm, and tension rate, and the reinforcement and elongation (average of five test pieces) at the time of fracture were searched for.

[0037] (8) a ratio -- the melt indexer made from a melt viscosity Oriental energy machine was used, after filling up with the 5g powder sample the cylinder with a bore of 9.53mm held at 372 degrees C \*\*1 degree C and holding it for 5 minutes, it extruded through the orifice with a bore [ of 2.1mm ], and a die length of 8mm under the 5kg load (a piston and weight), and the knockout rate at this time (a part for g) was found. a ratio -- melt viscosity was computed by the following formula.

a ratio -- melt viscosity  $\eta$  (poise) = 53150 / extrusion rate (a part for g)

[0038] (9) No-load melting fluidity (F)

The disc-like test piece of diameter 25(D0) mm pierced from 2mm sheet in thickness which carried out melting compression molding and obtained the powder non-constituent at 370 degrees C, and thickness 2(t) mm is placed on a mild steel plate with a thickness of 1mm ground with the sandpaper of #600, and after heating for 30 minutes at 310 degrees C all over a hot blast circulating reactor, it heats at 360 degrees C for further 1 hour. Subsequently, the mild steel plate which carried the test piece is cooled radiationally from a furnace to an ejection room temperature. It fuses, the diameter (D1) of the spreading test piece is measured, and the no-load melting fluidity F is computed by the degree type.

$F = (D1 - D0) / 2t$  [0039] (10) Marginal melting fluidity (f)

a ratio [ in / by the following formula / 372 degrees C of a powder constituent ] -- the f value and the above (9) which computed from melt viscosity  $\eta$  and were obtained Size with the F value of the obtained location survey was compared. (this invention constituent  $F \geq f$ )

$\log 10 f = 3.12 - 0.70 \log 10 \eta$  [0040] examples 1-4, the [examples 1-2 of comparison] mean particle diameter of 0.2 microns, the PPVE content of 3.4 % of the weight, the melting out temperature of 308 degrees C, and a ratio -- melt viscosity  $4.0 \times 10^4$  while agitating to the aqueous dispersion liquid of PFA of a poise -- a nitric acid -- subsequently trichlorofluoroethane was added, the end of agglomerated powder was obtained, and this was dried at 150 degrees C for 10 hours. In this way, it is 1 weight section and a thermoset stabilizer, respectively about PTFE powder A-E shown in the obtained desiccation powder 99 weight section and a table 2. After supplying the PPS ( "Ryton" made from TOSOH SASUTIRU V-1 grinding article) powder 1 weight section, and the pure-water 15 weight section to the Henschel mixer (FM10 made from Mitsui Miike chemically-modified opportunity B mold) and mixing for 10 minutes by 3000rpm, the trichlorofluoroethane 50 weight section was added small quantity every, it agitated for

1 minute by 1000rpm, and granulation powder was obtained. Subsequently, after heat-treating this at 300 degrees C for 10 hours, it classified with the screen of 1000 microns of openings, and the powder constituent of a passing sieve was made into the sample. The property of the test piece obtained from this powder constituent and it is shown in a table 3 with the result of the example of a comparison which does not add PTFE powder. The test piece obtained from the powder constituent which added a PTFE additive-free thing and small PTFE of the heat of crystallization was inferior in surface smooth nature. In addition, the mean particle diameter of the powder which supplied only the desiccation agglomerated powder end of above PFA to the Henschel mixer, processed for 10 minutes and was obtained by 3000rpm was 8 microns.

[0041] examples 5-13, the [examples 3-5 of comparison] mean particle diameter of 0.2 microns, the PPVE content of 3.5 % of the weight, the melting out temperature of 307 degrees C, and a ratio -- melt viscosity  $3.8 \times 10^4$  The powder constituent was obtained like the example 1 with the PTFE addition shown in a table 4 and a table 5 using the aqueous dispersion liquid of PFA of a poise, and the PTFE powder A. The property of a powder constituent and a test piece is shown in a table 4 and a table 5. the constituent which added PTFE to the large quantity -- a ratio -- the surface smooth nature of the test piece which it became difficult to fabricate a test piece and was obtained with the relative low therefore no-load melting fluidity to melt viscosity worsens.

[0042] an example 14, the [example 6 of comparison] mean particle diameter of 0.2 microns, the PPVE content of 3.5 % of the weight, the melting out temperature of 307 degrees C, and a ratio -- melt viscosity  $13 \times 10^4$  The aqueous dispersion liquid of PFA of a poise and the PTFE powder A were used, and the powder constituent was obtained like the example 1 so that the rate of PTFE in a pitch might become 0.5 % of the weight. The property of the test piece obtained from this powder constituent and it is shown in a table 6 with the result of the example of a comparison which does not add PTFE powder.

[0043] an example 15, the [example 7 of comparison] mean particle diameter of 0.2 microns, the PPVE content of 3.1 % of the weight, the melting out temperature of 308 degrees C, and a ratio -- melt viscosity  $33 \times 10^4$  The aqueous dispersion liquid of PFA of a poise and the PTFE powder A were used, and the powder constituent was obtained like the example 1 so that the rate of PTFE in a pitch might become 0.5 % of the weight. The property of the test piece obtained from this powder constituent and it is shown in a table 6 with the result of the example of a comparison which does not add PTFE powder.

[0044] After adding to the aqueous dispersion liquid of PFA which used the aqueous dispersion liquid F of PTFE of the mean particle diameter of 0.2 microns, and 34J/g of heat of crystallization which are the raw material of examples 16-20 and the [examples 8-10 of comparison] marketing "fine powder" in the example 1 so that the rate of PTFE in a pitch may become 0.001 - 1 % of the weight, and adding PPS powder at 1% of the weight of a rate to a pitch to them further, while agitating The nitric acid was added, the emulsion was destroyed, subsequently trichlorofluoroethane was added and churning granulation was carried out. Thus, after rinsing the obtained granulation powder and carrying out desiccation heat weld at 300 degrees C for 10 hours, the powder constituent was obtained by classifying with the screen of 1000 microns of openings. The property of a powder constituent and a test piece is shown in a table 7 with the result of the example of a comparison which did not add PTFE powder for the same actuation, but was carried out.

[0045] To the [example 21] mean particle diameter of 0.13 microns, and the aqueous dispersion liquid of PFA which used the aqueous dispersion liquid G of PTFE of heat-of-crystallization 47 J/g in the example 1, it added so that the rate of PTFE in a pitch might become 1 % of the weight, and the powder constituent was obtained like the example 16 to them. The property of a powder constituent and a test piece is shown in a table 8.

[0046] [An example 22, the example 11 of a comparison] (surface roughness test of the electrostatic-coating film)  
The 99.5 weight sections and the PTFE powder A 0.5 weight section were supplied to the Henschel mixer in the agglomerated powder end of PFA dried at 150 degrees C by the example 1, and granulation powder was obtained like the example 1. After heat-treating this granulation powder at 290 degrees C for 4 hours, it ground by rotational frequency 10000rpm using the ultracentrifuge mill (ZM made from RETCH- 1). The screen and the powder constituent of a passing sieve were obtained by 150 microns of backward openings which heat-treated this end of a pulverized powder at 300 degrees C for 6 hours. Electrostatic blasting of this powder constituent was carried out on the aluminum plate, it calcinated for 30 minutes at 360 degrees C, and the paint film with a thickness of about 80 microns was obtained. The property of a powder constituent and the surface roughness of a paint film are shown in a table 9 with the result of the example of a comparison which did not add PTFE powder for the same actuation, but was carried out.

[0047] [An example 23, the example 12 of a comparison] (surface roughness test of a revolution lining side)  
The powder constituent was obtained like the example 14 except not adding PPS. Revolution lining of a steel pipe inner surface was carried out according to the following conditions using this powder constituent. The same actuation is shown in a table 10 with the result of the example of a comparison which did not add PTFE powder for the property of a powder constituent, and the surface roughness of a lining side, but was carried out.

[0048] Metal mold: 3B black steel pipe (the bore of 80mm, die length of 150mm)

# 60 alumina sandblasting processing resin input: 200g (thickness of about 2mm)

Making machine: Product made from Tamagawa Machine Biaxial 100L rotational casting machine revolution 3.5rpm Rotation

5.0rpm baking conditions: 300->320 degrees C 320 degrees C of 5-minute temperature up 30 minutes [ of maintenance ]

320->360 degrees C 360 degrees C of 5-minute temperature up Maintenance 180-minute air cooling 20 minutes [0049]

[A table 3]

		比較例	実 施 例				比較例
番 号		1	1	2	3	4	2
PFAの種類		a (比溶解粘度 $4.0 \times 10^4$ ポイズ)					
PTFEの種類		無添加	A	B	C	D	E
粉 末 組 成 物 試 験 片	PTFE含有量 wt%	0	1	1	1	1	1
	PPS含有量 wt%	1	1	1	1	1	1
	平均粒径 ミクロン	375	405	400	400	435	390
	比溶解粘度 $\times 10^4$ ポイズ	4.0	4.1	3.9	5.9	4.0	4.4
	限界溶解流動度 f (計算値)	0.8	0.8	0.8	0.6	0.8	0.7
	無荷重溶解流動度 F (実測値)	1.7	1.7	1.7	1.6	1.7	1.7
	平均球粒径 ミクロン	65	3	5	6	8	45
試験片		平均粗さ ミクロン	0.5	0.1	0.1	0.1	0.7

[0050]

[A table 4]

		比較例	実 施 例				
番 号		3	5	6	7	8	9
PFAの種類		b (比溶解粘度 $3.8 \times 10^4$ ポイズ)					
PTFEの種類		A	A	A	A	A	A
粉 末 組 成 物 試 験 片	PTFE含有量 wt%	0	0.001	0.01	0.1	0.5	1
	PPS含有量 wt%	1	1	1	1	1	1
	平均粒径 ミクロン	385	395	410	385	370	370
	比溶解粘度	3.8	3.8	3.8	3.8	3.8	3.9
	限界溶解流動度 (計算値)	0.8	0.8	0.8	0.8	0.8	0.8
	無荷重溶解流動度 (実測値)	1.8	1.8	1.8	1.8	1.8	1.7
	平均球粒径 ミクロン	40	15	7	5	4	4
試験片	平均粗さ ミクロン	0.4	0.2	0.1	0.1	0.1	0.1
	引張強度 $\text{kgf/cm}^2$	320			290		280
	引張伸び %	420			390		400

[0051]

[A table 5]

		実 施 例				比 較 例	
番 号		10	11	12	13	4	5
PFAの種類		b (比溶解粘度 $3.8 \times 10^4$ ポイズ)					
PTFEの種類		粉末A ( $T_c = 316^\circ\text{C}$ , $H_c = 58\text{J/g}$ )					
粉 末 組 成 物 試 験 片	PTFE含有量 wt%	2	5	10	20	30	50
	PPS含有量 wt%	1	1	1	1	1	1
	平均粒径 ミクロン	390	420	400	370	400	380
	比溶解粘度	3.9	4.4	4.8	5.9	11	27
	限界溶解流動度 (計算値)	0.8	0.7	0.7	0.6	0.4	0.2
	無荷重溶解流動度 (実測値)	1.6	1.3	1.1	0.7	0.1	0.0
	平均球粒径 ミクロン	3	3	3	3	3	3
試験片	平均粗さ ミクロン	0.1	0.1	0.1	0.2	0.5	*
	引張強度 $\text{kgf/cm}^2$	270	240	220	200	180	150
	引張伸び %	360	360	240	160	100	20

\* Carry out crack initiation and it is film formation impossible. [0052]

[A table 6]

		比較例	実施例	比較例	実施例
番 号		6	14	7	15
PFAの種類		c (比溶解粘度 $13 \times 10^4$ ポイズ)		d (比溶解粘度 $33 \times 10^4$ ポイズ)	
PTFEの種類		無添加	A	無添加	A
粉末組成物	PTFE含有量 wt%	0	0.5	0	0.5
	PPS 含有量 wt%	1	1	1	1
	平均粒径 ミクロン	221	228	390	395
	比溶解粘度 $\times 10^4$ ポイズ	13	13	33	33
	限界溶解流動度 (計算値)	0.3	0.3	0.2	0.2
	無荷重溶解流動度 (実測値)	1.2	1.2	0.6	0.6
試験片	平均球晶径 ミクロン	85	3	60	4
	平均粗さ ミクロン	0.5	0.1	0.4	0.1

[0053]

[A table 7]

		比較例	実 施 例						比 較 例
番 号		8	16	17	18	19	20	9	10
PFAの種類		a (比溶解粘度 $4.0 \times 10^4$ ポイズ)							
PTFEの種類		無添加	水性分散液F						
粉末組成物	PTFE含有量 wt%	0	0.001	0.005	0.01	0.05	0.1	0.5	1
	PPS含有量 wt%	1	1	1	1	1	1	1	1
	平均粒径 ミクロン	405	410	390	365	380	405	395	390
	比溶解粘度 $\times 10$ ポイズ	4.0	4.0	4.0	4.1	4.2	4.6	5.1	6.8
	限界溶解流動度 (計算値)	0.8	0.8	0.8	0.8	0.8	0.7	0.7	0.5
	無荷重溶解流動度 (実測値)	1.7	1.7	1.7	1.6	1.4	1.2	0.5	0.1
試験片	平均球晶径 ミクロン	65	13	7	5	4	3	2	2
	平均粗さ ミクロン	0.5	0.2	0.1	0.1	0.1	0.1	0.3	0.6

[0054]

[A table 8]

		実施例
番 号		21
PFAの種類		a ( $4.0 \times 10^4$ ボイズ)
PTFEの種類		水性分散液 G
粉末組成物	PTFE含有量 wt%	1
	PPS含有量 wt%	1
	平均粒径ミクロン	385
	比溶解粘度 $\times 10$ ボイズ	5.2
	限界溶解流動度 (計算値)	0.7
試験片	無荷重溶解流動度 (実測値)	0.8
	平均球品径 ミクロン	5
試験片	平均粗さ ミクロン	0.2

[0055]

[A table 9]

		比較例	実施例
番 号		11	22
PFAの種類		a ( $4.0 \times 10^4$ ボイズ)	
PTFEの種類		無添加	粉末 A
粉末組成物	PTFE含有量 wt%	0	0.5
	PPS 含有量 wt%	0	0
	平均粒径 ミクロン	39	36
	比溶解粘度 $\times 10^4$ ボイズ	4.0	4.0
	限界溶解流動度 (計算値)	0.8	0.8
試験片	無荷重溶解流動度 (実測値)	1.8	1.8
	平均球品径 ミクロン	65	4
試験片	平均粗さ (塗膜面) ミクロン	0.4	0.1

[0056]

[A table 10]

		比較例	実施例
番 号		12	23
PFAの種類		c ( $13 \times 10^4$ ボイズ)	
PTFEの種類		無添加	PTFE粉末 A
粉末組成物	PTFE含有量 wt%	0	0.5
	PPS 含有量 wt%	0	0
	平均粒径 ミクロン	378	402
	比溶解粘度 $\times 10^4$ ボイズ	13	13
	限界溶解流動度 (計算値)	0.3	0.3
試験片	無荷重溶解流動度 (実測値)	1.2	1.2
	平均球品径 ミクロン	85	4
試験片	平均粗さ ミクロン (ライニング面)	0.6	0.1